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Online discrimination of chemical substances using standoff laser-induced fluorescence signals

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Abstract

Chemical contamination of objects and surfaces, caused by accident or on purpose, is a common security issue. Immediate countermeasures depend on the class of risk and consequently on the characteristics of the substances. Laser-based standoff detection techniques can help to provide information about the thread without direct contact of humans to the hazardous materials. This article explains a data acquisition and classification procedure for laser-induced fluorescence spectra of several chemical agents. The substances are excited from a distance of 3.5 m by laser pulses of two UV wavelengths (266 and 355 nm) with less than 0.1 mJ per laser pulse and a repetition rate of 100 Hz. Each pair of simultaneously emitted laser pulses is separated using an optical delay line. Every measurement consists of a dataset of 100 spectra per wavelength containing the signal intensities in the spectral range from 250 to 680 nm, recorded by a 32-channel photo multiplying tube array. Based on this dataset, three classification algorithms are trained which can distinguish the samples by their single spectra with an accuracy of over 98%. These predictive models, generated with decision trees, support vector machines, and neural networks, can identify all agents (eg, benzaldehyde, isoproturon, and piperine) within the current set of substances.

KEYWORDS

chemical agents, classification algorithms, laser-induced fluorescence, machine learning, standoff detection

1 | INTRODUCTION

When people or buildings are chemically contaminated, time is a valuable factor for the success of first responders. A fast determination of the hazardous substances is essential for an initialization of specific counter measures. In situ analyses save transportation time but need access to the hotspot. Avoiding this, standoff measurements are more secure for operators but due to the distance in general less sensitive concerning distinctive results.

There are many different technologies that can be used for laser-based standoff detection. The most prominent methods are light detection and ranging (LIDAR), differential absorption LIDAR (DIAL), infrared (IR), laser-induced

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breakdown (LIBS), Raman, and laser-induced fluorescence (LIF) spectroscopy.[1-3] Within these techniques, LIF provides the advantage of high sensitivity, and most materials absorb radiation in the ultraviolet (UV) spectral region and, depending on the internal structure, may emit fluorescence radiation after excitation. But the selectivity of this technique is rather limited. For biological samples containing different fluorophores, it can be increased by using additional wavelengths for excitation because thereby different fluorophores can be excited, gaining more information from the examined samples.[4] This is also the case for mixtures of chemicals like diesel.[5] For the classification of chemicals, Raman or IR spectroscopy is used most dominantly, and little work has been done on the standoff detection of explosives or chemical agents using fluorescence spectroscopy.[3] An interesting approach was made for a setup by utilizing a combination of LIF and Raman spectroscopy for chemical and biological sensing.[6,8]

All these techniques provide the usage of machine learning algorithms to analyze the data. Speed, neutrality, and performance are some of the advantages of artificial intelligence techniques when large datasets with a high-dimensional structure have to be classified. Such computing is used in almost every research area, and the development is promising, including the purpose of standoff detection.[8-12]

Within this scope, a data analysis is presented, where laser-induced fluorescence spectra of 20 different chemical substances are classified, and the results of different algorithms, like decision trees (eg, C5.0), support vector machine (SVM), and artificial neural network (ANN), is evaluated.

TABLE 1 This list indicates the substances which are measured with the current LIF setup and subsequently discriminated by their spectra. Liquids are measured pure; solids are dissolved either in water or diethyl ether depending on their solubility

Fuel	Lubricant	Pesticide	Solvent
Diesel	Anderol555	Imidacloprid(w)	Benzaldehyde
Jet fuel	Motor oil	Isoproturon(d)	Cyclopentan
Kerosene		Malathion(w)	Ethyl acetate
Paraffin		Oxyfluorfen(d)	Isopropyl alcohol
		Permethrin(d)	Losin100
		Terbuthylazine(d)	p-Xylol
		Piperine(w)	Turpentine substitute

Pure liquid substances; pesticides dissolved in water (w) or diethyl ether (d).

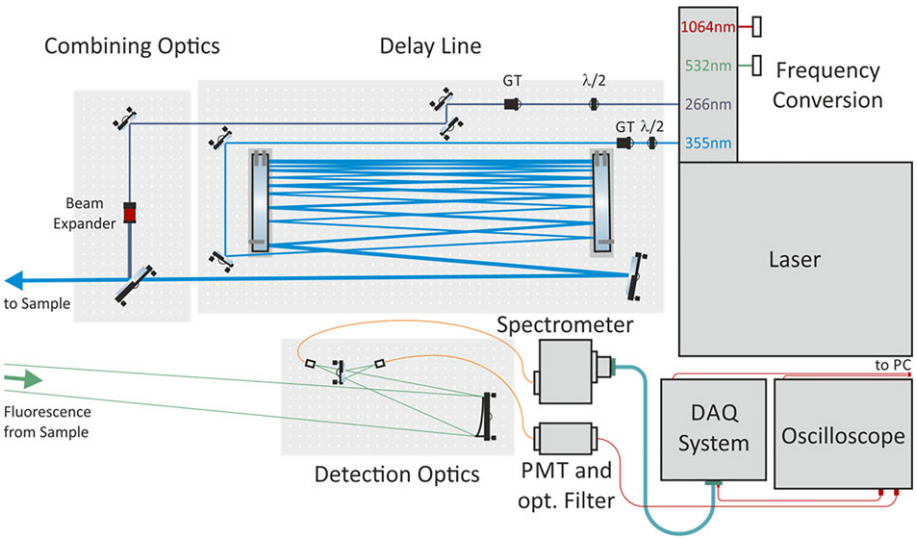

FIGURE 1 Schematic view of the experimental setup showing all important components, the optical paths of the excitation pulses (blue and purple), and the detectable fluorescence signal (green)

2 | MATERIALS AND METHODS

2.1 | Experimental

Depending on the scenario, there can be many kinds of pollution and background materials which are worth being identified. Within this work, the discrimination of an example set of 20 different substances is described which represent four groups of chemicals (fuels, lubricants, pesticides, and solvents) as shown in Table 1. Liquid samples are measured in pure condition, and solids are dissolved in water or, if required, in diethyl ether. All probes are filled in colloidal 3.5-mL glass cuvettes, excited 3.5 m apart, and stirred during the measurements.

The laser system in Figure 1 was described in detail in a previous work,[13] so only a short summary of the main components is presented here. LIF is excited by frequency converted laser pulses of a Nd:YAG laser (InnoLas Picolo Magna EVO III) with wavelengths of 266 and 355 nm, pulse widths of 0.7 ns (FWHM), and a repetition rate of 100 pulses per

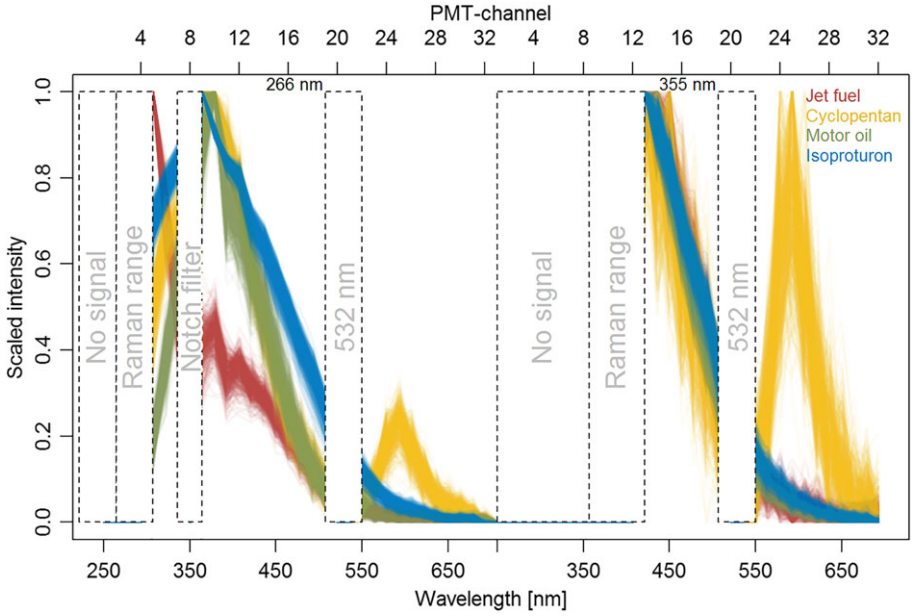

FIGURE 2 Normalized LIF spectra of four representative substances showing the regions of eliminated channels

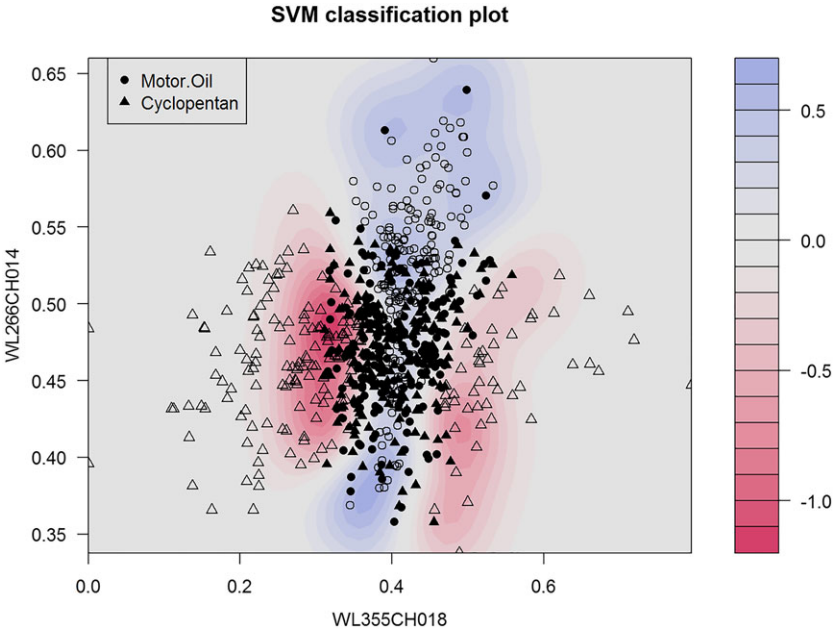

FIGURE 3 As an example, this SVM model separates two of the substances using only two features. In hyperspace, on which the kernel function maps to, the curvy borders are planes

TABLE 2 All training computations are performed with RStudio[19] and the function train() from the caret package. A summary of settings and results is given in this brief overview. More details about the models and their specific tuning parameters can be found in the package documentations

Training options			
Method name	C5.0	svmRadial	pcaNNet
Additional package	C50	kernlab	nnet
Resampling	Cross-validation	Bootstrap	Bootstrap
	(10-fold)	(5 repetitions)	(5 repetitions)
Feature selection	No	No	PCA
Nominal settings	Pruning	Gaussian kernel	One hidden layer
	minCases = 2		Sigmoid activation
	CF = 0.25		Iteration limit: 1000
Tuning parameters			
	.trials (iterations)	.sigma (kernel width)	.size (hidden units)
		.C (cost factor)	.decay (weight update term)
Results			
Best tune	trials = 25	sigma = 0.5	size = 12
		C = 1.5	decay = 0.1
Accuracy	0.9904	0.9892	0.9952
Kappa	0.9899	0.9886	0.9949
Important features	(model specific)	(model independent)	(model independent)
	WL266CH015	WL266CH005	WL266CH005
	WL355CH026	WL266CH006	WL266CH006
	WL266CH014	WL266CH007	WL266CH007
Training time	4′52″	23′40″	1°5′45″

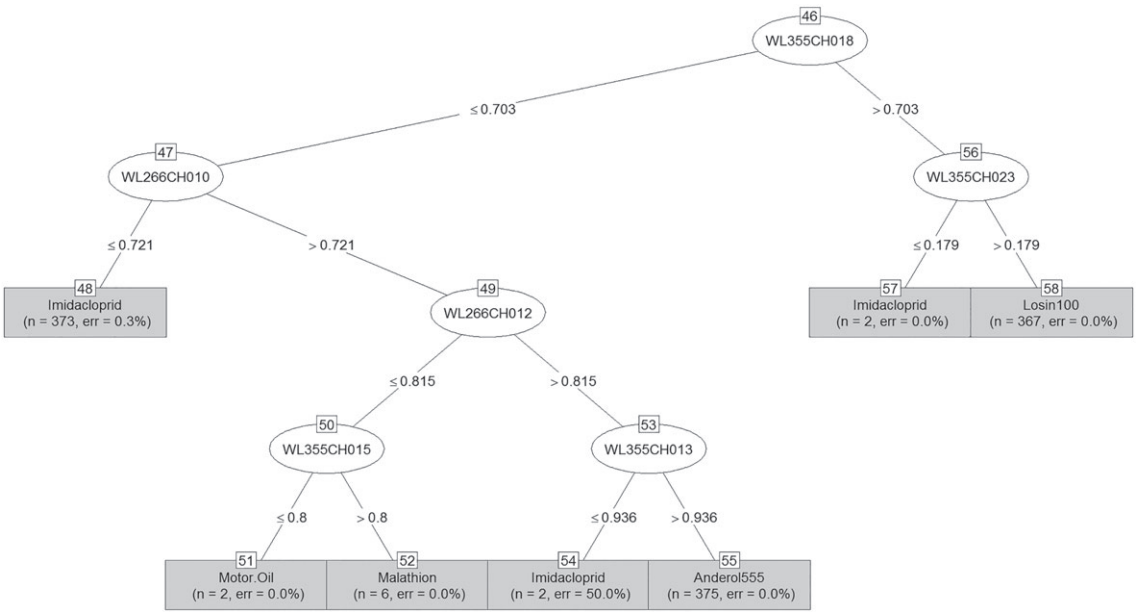

FIGURE 4 A subtree of the C5.0 model has been chosen to visualize some of the splitting rules

second. These conditions enable pulse energies up to 60 mJ required for larger distances. Depending on the fluorescence intensity, energies are adjusted between a few 10 nJ up to 200 μJ using a polarizer and a half-wave plate. To gain independent excitation, the 355-nm pulse is delayed by approximately 100 ns to the 266 nm one by multiple reflections between two mirrors which are slightly tilted with respect to each other. Afterwards the optical paths are united and guided onto the target. The resulting fluorescence signals are collected by an off-axis parabolic mirror with a diameter of 10.2 cm (Edmund Optics #83-957) focusing the radiation onto the input facet of an optical fiber that guides the signal to a grating-based spectrometer (Hamamatsu A10766). There, the radiation is diffracted onto a photomultiplier tube (PMT) array with 32 channels spanning a spectral range from 250 to 680 nm. For the electronic signals of each excitation, an integration time of 50 ns is achieved by a high-speed data acquisition system (Vertilon's PhotoniQ).

The measurements are performed indoors, and each dataset, containing 100 background corrected LIF signals with 32 channels per excitation wavelength (266 and 355 nm), can be recorded in less than 2 seconds. Every chemical is measured five times which results in 500 spectra per substance, yielding an overall dataset of 10 000 labeled spectra with 64 features for the following data analysis.

2.2 | Data preprocessing

The spectra still contain undesirable signals which are deleted for not affecting scaling or classification processes. Therefore, the spectroscopic background signals below the excitation wavelengths are eliminated (channels 1 to 2 and

TABLE 3 This confusion matrix shows predictions of *C5.0* applied on the test set with an accuracy of 99.1%

Prediction \ Reference	Anderol555	Benzaldehyde	Cyclopentan	Diesel	Ethyl acetate	Imidacloprid	Isopropyl alcohol	Isoproturon	Jet fuel	Kerosene	Losin100	Malathion	Motor oil	Oxyfluorfen	p-Xylol	Paraffin	Permethrin	Piperine	Terbuthylazine	Turpentine substitute
Anderol555	125																			
Benzaldehyde		124																		
Cyclopentan			125																	
Diesel				125																
Ethyl acetate					120							2								
Imidacloprid						125														
Isopropyl alcohol							125													
Isoproturon								120						1			4			
Jet fuel					1				125											
Kerosene										125										
Losin100											125									
Malathion		1			4							123								
Motor oil													125							
Oxyfluorfen														123			3			
p-Xylol															123					
Paraffin															2	125				
Permethrin								5						1			118			
Piperine																		125		
Terbuthylazine																			125	
Turpentine substitute																				125

channels 1 to 7, respectively) as well as channel 8 in the spectral region of the notch filter which blocks the reflected radiation at a wavelength of 355 nm.

In addition, Raman peaks may occur in adjacent regions of the excitation wavelength. Within this set of substances, the largest shifts are expected in a wavenumber range from 3200 to 3600 cm^{-1}, corresponding to vibrations in water. The associated peak positions are at 292 and 405 nm, respectively. The concerned features including potential Raman peaks are channels 3 and 4 in the 266-nm signals and channels 9 to 12 in the 355-nm signals—and thus are eliminated.

Furthermore, some spectra of low intensity show a slight elevation around 532 nm, which is caused by a remaining signal of the second harmonic output of the laser. So, for both excitation wavelengths, the according two channels are set to zero. For reasons of comparability, the spectra are range scaled from 0 to 1. The resulting dataset with the remaining 43 relevant channels is visualized for four substances in Figure 2.

2.3 | Classification

Classification models serve the purpose to predict an outcome for new data based on well-known observations. Their development mainly consists of two steps called training and test which are performed with two parts of a given dataset. Here, 75% of the data are used as training set to learn how to distinguish the spectra as good as possible according to

TABLE 4 This confusion matrix shows predictions of *svmRadial* applied on the test set with an accuracy of 98.9%

Prediction \ Reference	Anderol555	Benzaldehyde	Cyclopentan	Diesel	Ethyl acetate	Imidacloprid	Isopropyl alcohol	Isoproturon	Jet fuel	Kerosene	Losin100	Malathion	Motor oil	Oxyfluorfen	p-Xylol	Paraffin	Permethrin	Piperine	Terbuthylazine	Turpentine substitute
Anderol555	125																			
Benzaldehyde		124																		
Cyclopentan			125																	
Diesel				125																
Ethyl acetate		1			125							1								
Imidacloprid						125														
Isopropyl alcohol							125													
Isoproturon								119									4			
Jet fuel									125											
Kerosene										125										
Losin100											125									
Malathion												124								
Motor oil													125							
Oxyfluorfen								2						122			4			
p-Xylol															125	8				
Paraffin																117				
Permethrin								4						3			117			
Piperine																		125		
Terbuthylazine																			125	
Turpentine substitute																				125

their labels. Afterwards, predictions are made for the remaining test set to evaluate the goodness of fit of the previously learned model according to its accuracy, ie, the proportion of correctly and totally predicted spectra.

For this work, the discrimination of the substances is investigated by making use of three different classification methods. The decision tree algorithm *C5.0* extracts distinctive features which separate the spectra and calculates optimal benchmarks for its decisions. The so constructed borders between the intensity values of different signals are rearranged by minimizing the distances. Finally, the tree is pruned by eliminating redundant branches.[14,15]

Support vector machines (SVM) map the data onto a hyperspace where two respective features of the signals can be separated linearly considering only adjacent points of different classes which are called support vectors. The final model is created by a simultaneous mapping of all channels, a division of all substances, and a subsequent back transformation.[16] As an example, a subspace of a model which separates two of the substances is visualized in Figure 3.

An ANN consists of multiple linear combinations of features which are linearly combined in one or more hidden layers. The coefficients (or weights) of every combination are the result of iteration and backpropagation which are explained in miscellaneous articles and books.[15,17,18]

Additional resampling methods like k-fold cross-validation or bootstrapping in the partitioning step as well as in the training should be included to ensure less overfitted models, more valid for future observations.

While applying specific methods on specific data, the search for optimal parameters is like looking for a needle in a haystack. This process (called *tuning*) is often discussed because of its pitfalls like iterating to local optima without global consideration. Otherwise, it is not sensible and mostly not even possible to check every parameter combination.

TABLE 5 This confusion matrix shows predictions of pcaNNet applied on the test set with an accuracy of 99.6%

Prediction \ Reference	Anderol555	Benzaldehyde	Cyclopentan	Diesel	Ethyl acetate	Imidacloprid	Isopropyl alcohol	Isoproturon	Jet fuel	Kerosene	Losin100	Malathion	Motor oil	Oxyfluorfen	p-Xylol	Paraffin	Permethrin	Piperine	Terbuthylazine	Turpentine substitute
Anderol555	125											1								
Benzaldehyde		124																		
Cyclopentan			125																	
Diesel				125																
Ethyl acetate		1			125															
Imidacloprid						125														
Isopropyl alcohol							125													
Isoproturon								123									2			
Jet fuel									125											
Kerosene										125										
Losin100											125									
Malathion												121								
Motor oil													125							
Oxyfluorfen												2		125			1			
p-Xylol															125	1				
Paraffin																124				
Permethrin								2				1					122			
Piperine																		125		
Terbuthylazine																			125	
Turpentine substitute																				125

In this work, a grid-based search was used which means that every tuning parameter is assigned to a limited set of values. The training is performed for every combination, and the model with the highest accuracy, when applied on the test set, is chosen.

3 | RESULTS AND DISCUSSION

For the *C5.0*, the number of iterated decision trees was the only tuning parameter. The minimal number of cases for each split was held constant and also the confidence factor (CF) which affects the severity of pruning (see Table 2). Applying the model on the test set results in an accuracy of 99.0%. Figure 4 shows only a subtree of the final model. The full tree is too complex.

Using a Gaussian kernel, the SVM model was generated by tuning the kernel width and the cost parameter C which penalizes large residuals and influences the variance in the model.[15] The final prediction has an accuracy of 98.9%.

With a preceding principal component analysis and one hidden layer with 12 units, the ANN model reaches 99.5%. Here, weight decay and the number of hidden units were varied to tune the model. "*Weight decay*, specific to neural networks, uses as penalty the sum of squares of the weights w_{ij}. (This only makes sense if the inputs are rescaled to range about [0, 1] to be comparable with the outputs of internal units.) The use of weight decay seems both to help the optimization process and to avoid over-fitting".[17] This is also a good justification for the use of range scaling in data preprocess.

The confusion matrices for all three classifications of the test set are shown in Tables 3–5. They show an almost perfect discrimination of all substances. Most of the errors occur especially in the context of Permethrin, but the reasons for that behavior were not further examined yet. According to each substance and model, the sensitivity and specificity are presented in Table 6. Within a measurement of 100 single signals, there are at most 10 spectra which are misclassified.

TABLE 6 For each substance and every method, the sensitivity and specificity are indicated as follows. Sensitivity is the ratio of correctly assigned spectra to the real amount of substance spectra. Specificity is the ratio of spectra of the remaining substances, which are correctly classified as another substance, to the real amount of spectra of other substances

Method	C5.0		svmRadial		pcaNNet	
Statistic	Sensitivity	Specificity	Sensitivity	Specificity	Sensitivity	Specificity
Anderol555	1.000	1.000	1.000	1.000	1.000	1.000
Benzaldehyde	0.992	1.000	0.992	1.000	0.992	1.000
Cyclopentan	1.000	1.000	1.000	1.000	1.000	1.000
Diesel	1.000	1.000	1.000	1.000	1.000	1.000
Ethyl acetate	0.960	0.999	1.000	0.999	0.992	1.000
Imidacloprid	1.000	1.000	1.000	1.000	1.000	1.000
Isopropyl alcohol	1.000	1.000	1.000	1.000	1.000	1.000
Isoproturon	0.960	0.998	0.952	0.998	0.976	0.999
Jet fuel	1.000	1.000	1.000	1.000	1.000	1.000
Kerosene	1.000	1.000	1.000	1.000	1.000	1.000
Losin100	1.000	1.000	1.000	1.000	1.000	1.000
Malathion	0.984	0.998	0.992	1.000	0.992	1.000
Motor oil	1.000	1.000	1.000	1.000	1.000	1.000
Oxyfluorfen	0.984	0.999	0.976	0.997	1.000	0.999
p-Xylol	0.984	1.000	1.000	0.997	0.992	1.000
Paraffin	1.000	0.999	0.936	1.000	0.992	1.000
Permethrin	0.944	0.997	0.936	0.997	0.968	0.999
Piperine	1.000	1.000	1.000	1.000	1.000	1.000
Terbuthylazine	1.000	1.000	1.000	1.000	1.000	1.000
Turpentine substitute	1.000	1.000	1.000	1.000	1.000	1.000

All described computations are operated on a desktop PC (Intel Xeon E5-1630 v4, 3.7 GHz, 32 GB RAM) using *R* version 3.4.4[20] and mainly the packages *C50,*[14] *kernlab,*[16] *nnet*,[17] and *caret*.[21] The latter enables resampled partitioning and the use of several classification algorithms within a consistent data structure.

4 | SUMMARY AND OUTLOOK

The results show that LIF spectra of various chemicals can be separated with these different methods of machine learning techniques. All of the described algorithms are able to distinguish the spectra with a very good performance of around 99%. For online execution, a trained model will be implemented in the setup after the data acquisition system gaining a prediction of the measured substance within just a few seconds in total. With a maximum of 10 misclassifications per measurement consisting of 100 spectra, this procedure for online discrimination of chemical substances seems feasible.

Present and future experiments will be performed outdoor at distances up to 130 m on a laser test range operated by the German Aerospace Center (DLR) in Lampoldshausen, Germany. For a promising recognition of all examined materials, new measurements will be investigated with lower concentrations as well as various backgrounds or mixtures of different ratios, and these data have to be taken into account for the modeling process. Due to expected additional influences from atmosphere, a combination of miscellaneous algorithms or a multilevel classification might be the key to extend the limits of detection, to low error rate and to high sensitivity.

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